OPTICAL TRANSMISSION OF CASSITERITE AS A FUNCTION OF TEMPERATURE

By

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CHAPTER I

INTRODUCTION

Optical transmission measurements provide a standard method of determining some of the fundamental parameters of a semiconductor. One of these parameters is the value of the forbidden energy gap. Without a knowledge of this value a complete theoretical consideration of the conduction mechanism is impossible. One purpose of this optical study, then, was to obtain information leading to a reasonably accurate value of the minimum energy gap of cassiterite which is the natural crystalline form of stannic oxide. In addition, it was designed to investigate the variation of the proposed energy gap with temperature, to locate significant absorptions, if any, in the wavelength range from 0.35 to 4.0 microns and to study in particular a characteristic sharp absorption previously noted near 3.1 microns. The information gained forms a portion of a broad experimental program which has as its ultimate aim the proposal of an energy level diagram for cassiterite.

Although a number of oxides have been studied rather extensively in regard to their semiconducting properties in the last few years, little has been done with cassiterite. A comprehensive review of the literature on semiconducting oxides as well as a discussion of the crystal structure of stannic oxide has been presented by Hurt (1) and Northrip (2). Therefore, only those articles and properties pertaining directly to this study will be reiterated.

Rutile - titanium dioxide - which has the same crystal structure as cassiterite has been under investigation for a number of years. In particular, several studies have been carried out on its optical properties (3, 4). Since cassiterite is of a similar structure it might be expected that its optical properties may also be similar. Therefore, a brief resume of the most significant optical work done on TiO_2 follows.

Cronemeyer (3) conducted a study of the optical absorption edge of TiO_2 from 0.40 to 0.54 microns between 4.2° and 775° K. He found a shift of the band edge toward lower energies at the rate of 6.3×10^{-4} ev/°K, for an absorption coefficient of 30 cm^{-1}. However, he found an exception in that there was an anomalous shift toward longer wave lengths as the temperature approached 4° K. Upon closer investigation the anomaly was explained by a secondary absorption in addition to the fundamental absorption masking the band edge and thus causing the apparent shift as the temperature was reduced. It was also noted that the optical absorption edge sharpened toward low temperatures. He reported an average value of 3.05 ev for the optical band separation.

Soffer (4) conducted a study in which he investigated the optical absorption spectrum of single crystals of synthetic rutile in the spectral range from 1,200 to 25,000 cm^{-1} (8.33 to 0.4 microns) at temperatures ranging from room temperature to 1,000° C. He found that the electronic absorption exhibited dichroic behavior. The edge moved toward lower energies as the temperature was increased, with the shift depending upon the absorption coefficient. For a decadic absorption coefficient of 400 cm^{-1} the shift was -7.1×10^{-4} ev/°K. He also found new absorption bands in the 3300 cm^{-1} (3.03 micron) region. These consisted of two sharp absorptions at 3277 and 3322 cm^{-1} (3.051 and 3.01 microns), the

former being the more intense of the two. He demonstrated that the bands result from the presence of hydrogen in the lattice and correspond to O-H stretching vibrations. The splitting of the band was attributed to a weak hydrogen bonding.

Northrip (2) conducted optical measurements on several natural crystals of stannic oxide. He found in general a value in the region of 0.355-0.360 microns for the short wavelength cutoff and an intense absorption in the region of 3.75 microns which was later corrected to 3.1 microns on the basis of instrument recalibration.

Hurt (1) investigated photoconductivity in the same crystals. He found that all samples investigated with the exception of those of very low resistivity showed measurable photoconductivity. Measurements were carried out over a wavelength region extending from 0.25 to 0.46 microns. He also succeeded in correlating the peak response of the most sensitive sample for one minute light exposures to the wavelength at thich the short wavelength cutoff was found.

Aitchison (5) measured transmission of layers of SnO_2 on glass, oxide crystal, and silicate crystal substrates. He conducted these measurements over a spectral range from 0.18 microns in the ultraviolet to 15 microns in the infrared, finding no strong absorption bands in this region. However, he indicated that the thin layers may have made the detection of absorption bands difficult.

Coblentz (6) in making infrared measurements on cassiterite found a number of shallow absorption bands occurring between 1.3 and 10.4 microns. However, his investigation was purely observational in character and no interpretations were attempted.

Ecklebe (7) studied the variation of the absorption edge of

cassiterite in the range between 400° and 1100° C. From his published curves the rate of shift of the edge can be estimated as -12×10^{-4} ev/°K.

During the course of the present study, several limitations were encountered. One of these is due to the form of the specimens available. All samples were obtained from natural crystals of cassiterite; therefore, there was no way of controlling their impurity content. Furthermore, attempts at crystal orientation had to be sacrificed in the interest of maximum uniformity, size, and transparency. A difficulty of another sort was presented by the limited knowledge of the index of refraction since its variation with wavelength is necessary in order to represent the data in terms of optical constants. Ecklebe (7) measured the index of refraction for cassiterite in the range from 0.444 to 0.715 microns and found a proper formula to fit the measured data for the ordinary ray. However, no measurements of the index of refraction in the range below 0.444 microns have been found and it should be noted that this is the critical region for determination of absorption constants near the short wavelength cutoff. Consequently, it is seen that a quantitative comparison of the optical data of cassiterite with that of rutile is impractical. However, by making some approximations it was found that a satisfactory qualitative comparison could be made.

In summation, this study reports the results obtained on five samples of natural cassiterite which were submitted to the same measurements. These consisted of optical transmission measurements conducted on a Beckman DK-1 Spectrophotometer from near 0.35 microns, the short wavelength cutoff, to 2.6 microns and on a Perkin-Elmer 12C Infrared Spectrometer from 2.6 to 4.0 microns. Data were obtained at three

different temperatures - liquid nitrogen temperature, room temperature, and 140° C. Two of the samples used had undergone special oxidation or reduction treatment. The general character of the transmission over the primary transparency region from the short wavelength cutoff to a long wavelength cutoff near 8 microns was observed at room temperature.

CHAPTER II

OPTICAL ENERGY GAP THEORY

One of the simplest cases of absorption occurs in a homogeneous absorbing medium in which a parallel beam of monochromatic radiation passes rectilinearly through the medium. In this instance the intensity is reduced by the same fractional amount in equal succeeding portions of its path. A mathematical representation of this effect, known as Lambert's law is given by $I_x = I_o e^{-\alpha x}$. The constant α is known as the absorption coefficient and represents the fraction by which absorption reduces the intensity in unit length of path. I_o is the intensity of the radiation that enters the absorbing medium and I_x is the intensity incident upon the exit face. The thickness of the medium is represented by x. In a practical situation I_o is not usually the same as the intensity I incident on the entrance face of a solid, nor is I_x the same as the intensity I' of radiation leaving the exit face. The reason for this may be due to several factors. The most prominent of these in the case of a solid is reflection of the radiation which reduced the intensity at all faces in a specimen. Other factors may be fluorescent radiation emitted by the absorbing medium, multiple reflections between the faces of a specimen, reflections from the sides of a specimen when the beam of radiant energy is not strictly parallel, and lack of homogeneity in the absorbing medium. The conditions of measurement should be so chosen that these effects are eliminated or reduced to a minimum in which case they may be considered

negligible. It is seen that reflection from the faces of the specimen cannot be eliminated entirely although the difficulty of correcting for it may be reduced by placing the sample face perpendicular to the incident radiation. This correction must then be taken into account if it is wished to determine the true transmittance T_o which is defined as the ratio of I_x to I_o. Actually the spectrophotometer measures the ratio of the intensity of the radiation I' leaving the exit face to that of the intensity of the incident radiation I. Therefore, in order to determine the absorption constant measured transmittance values must be corrected for reflection losses.

Moss (8) in considering transmission measurements on semiconductors gives the average measured transmittance as

$$T = (1-R)^2 e^{-\alpha x} \tag{1}$$

where R, the reflection coefficient, is given by

$$R = [(n-1)^2 + k^2] \; / \; [(n+1)^2 + k^2] \tag{2}$$

This is true for the medium adjacent to the sample being air or a vacuum and the absorbing medium having an index of refraction n. The term k is given by

$$k = \frac{\lambda \alpha}{4\pi} \tag{3}$$

For the wavelength region of interest, $k^2 \ll n^2$, so that the reflection coefficient reduces to

$$R = \frac{(n-1)^2}{(n+1)^2} \tag{4}$$

and the transmittance becomes in the first approximation

$$T = \left[1 - \frac{(n-1)^2}{(n+1)^2}\right]^2 e^{-\alpha x} \tag{5}$$

Solving this for α one obtains

$$\alpha = \frac{1}{x} \ln \left\{ \frac{1}{T} \left[\frac{2n}{(n+1)^2} \right]^2 \right\} \qquad (6)$$

Thus, if the thickness of the sample, x, is known and the variation of n with λ is known one may measure T and determine the absorption coefficient.

A characteristic feature of semiconductors in the pure state is that in a certain wavelength range the absorption coefficient falls rapidly and the material becomes rather transparent at longer wavelengths. This marked fall in absorption is called the fundamental absorption edge and is found to be due to an electronic transition. Although this description is useful, there arises the practical difficulty of specifically naming a wavelength defining the absorption edge of the particular material in question. However, it is essential to have a unique threshold value of photon energy, $h\nu$, to compare with the forbidden gap energy which may be determined from the thermal variation of conductivity or Hall constant. Even assuming a simple band structure, the sharpness of definition of this energy is usually limited by experimental difficulties arising from the fact that it is impossible to obtain an ideal or pure crystal. For example, impurities in a sample may well cause a variation in how rapidly the absorption coefficient drops. In the neighborhood of the edge the transmission may fall to such low values that it becomes difficult to separate the portion of the absorption which is due to band-to-band transitions from that due to the presence of defects.

Moss (8) defines a method of determining the edge. He indicates that the main parameter determining the absorption is the density of

allowed states, N(E), where E is the electron energy. This follows from an expression given by Fan (9) showing that the absorption coefficient is proportional to this quantity. In an ideal system N(E) will be a discontinuous function, i.e. in the case of the conduction band it will be finite for energies above the bottom of the band and zero for energies below. However, in the case of a practical system N(E) may not be discontinuous. It has been shown theoretically by Parmenter (10) that any lattice disorders cause a tailing-off of the density of allowed states curve into the forbidden zone. If this is the case, then it is reasonable to define the band edge at the wavelength where N(E) changes most rapidly with E, i.e. where $\frac{dN(E)}{dE}$ is a maximum. Correspondingly, then, the absorption edge may be defined as the point where the slope of the absorption coefficient is a maximum.

The wavelength, λ, and the frequency, ν, corresponding to this point are related approximately by the equation $h\frac{c}{\lambda} = h\nu = \Delta E$ where ΔE is the forbidden energy gap and is thus the energy required to excite an electron from the top of the valence band to the bottom of the conduction band. Since this transition is not always possible without involving other considerations the above equation must be modified to fit each particular situation. However, unless very precise measurements are available this usually is a good approximation.

CHAPTER III

INSTRUMENTATION AND MEASUREMENT TECHNIQUES

Apparatus

In this study it was found necessary to construct a transmission cell suitable for use at both low and high temperatures. In addition it was desirable to have a cell which would function properly on both the Beckman DK-1 Spectrophotometer and the Perkin-Elmer 12C Infrared Spectrometer. The basic principle of construction of the cell called for having the sample mounted on the lower end of a hollow cylindrical tube which could be filled with liquid nitrogen or heated gas depending upon the temperature desired. Enclosing tube and sample with a jacket and leaving an appreciable space between the inner tube and the outer jacket provided good thermal insulation when the space was evacuated. This was found necessary in low temperature experimentation in order to minimize drift problems which would be introduced if large temperature gradients were allowed to develop in the vicinity of the sample. Evacuation also reduced the possibility of sample contamination by water during the measurements.

Figure 1 shows the construction of the cell used. The inner part is the hollow cylindrical tube constructed of monel which serves as the coolant chamber in the case of low temperature measurements. Liquid nitrogen is introduced into the inlet tube while the exit tube serves as a means of releasing the vaporized gas. In the case of high

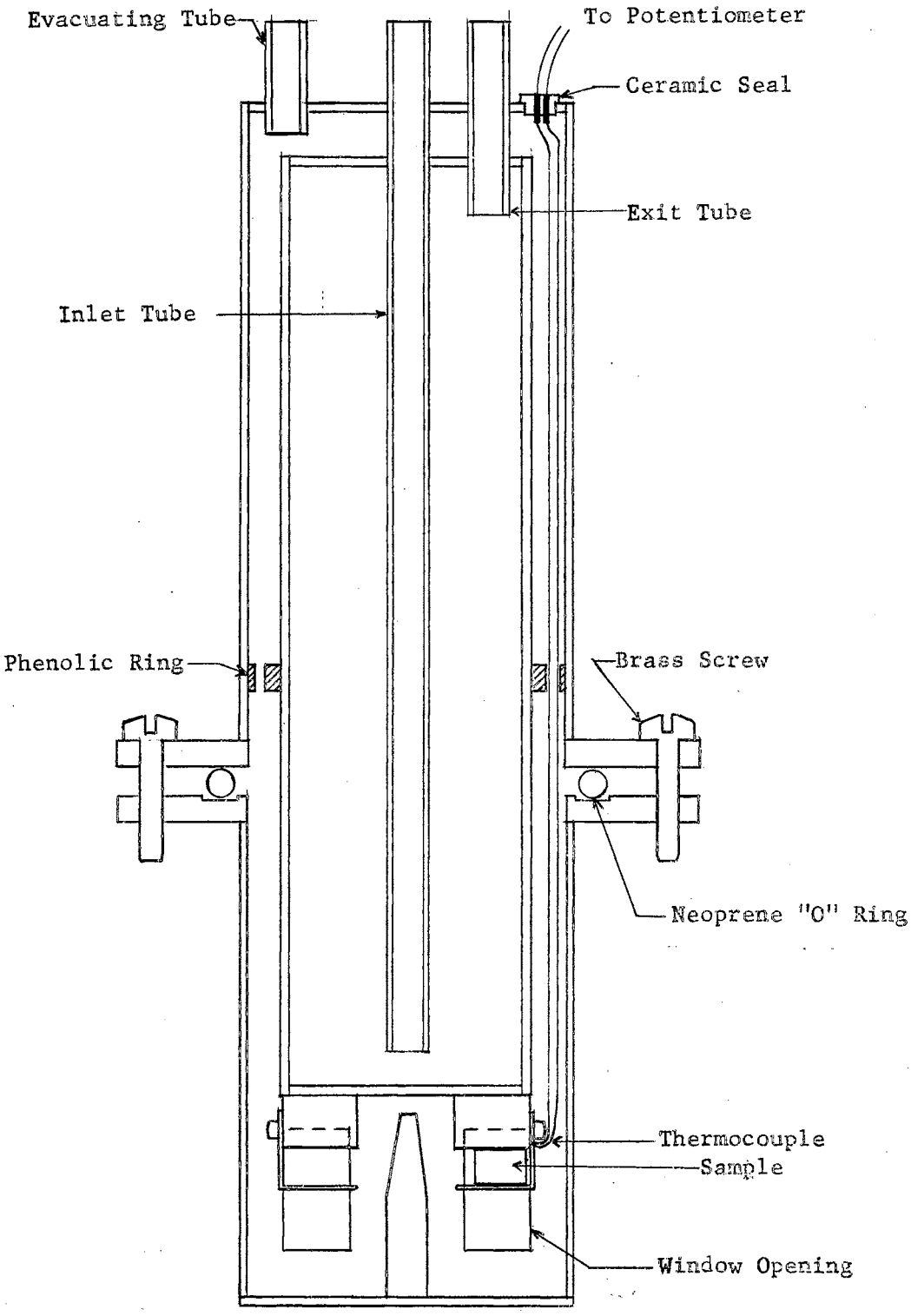

Figure 1. Cross Section of Sample Holder

temperature measurements the apparatus functions the same except that heated nitrogen gas is used.

On the bottom of the inner chamber two solid copper cylinders are attached. On one of these cylinders the sample to be investigated is mounted. The second cylinder provides a reference position when the holder is used in the DK-1 Spectrophotometer which is a double-beam instrument. The mounting of the sample is accomplished by means of the L-shaped holder which is also made of copper. The sample is placed between the holder and the copper cylinder and the holder is then fastened to the side of the cylinder by means of a screw. The screw hole located in the holder is slotted to facilitate mounting samples of various sizes. In addition the underside of the cylinder has a groove cut in it to help hold the sample while it is being mounted and to eliminate the possibility of light passing between the sample and the cylinder. Also fastened to the lower part of the copper cylinder is a copper-constantan thermocouple used for high and low temperature measurements alike.

The inner portion of the apparatus is then encased in a jacket. This jacket is also constructed of monel. It consists of two parts, an upper and a lower half. The upper half is permanently attached to the inner chamber by means of the inlet tube, the exit tube, and the evacuating tube. Separation is maintained by means of a phenolic ring. The lower half of the jacket is square-shaped to facilitate mounting of the windows and to fit the sample compartment of the spectrophotometer. The lower half is separated from the upper half by a neoprene "O" ring and the two halves are fastened together with six brass screws. Four fused quartz windows are used to cover the entrance and exit openings on the

lower half of the jacket. These are fastened with apiezon wax which, due to its high melting point, was found to be suitable for both low and high temperature measurements.

All surfaces on the inside of the lower half of the outer jacket and those on the outside of the lower portion of the coolant chamber were blackened to prevent reflection of any stray light.

It was also found necessary to place on the exit window a plate with an opening to insure that only the light passing through the sample was being detected by the instrument. In other words if no aperture were used and the sample was small a considerable amount of light might pass around it and be recorded thus giving an erroneous measurement.

All measurements using the above apparatus were made on the Beckman DK-1 Spectrophotometer and the Perkin Elmer 12C Infrared Spectrometer. These instruments have both been described as to operation and performance by Northrip (2) and no further general description is deemed necessary here. A number of preliminary room temperature measurements were obtained using the simple apparatus and procedure described by Northrip in the same reference.

Description of Samples

Complete experimental measurements were taken on five different samples. These were all cut with a diamond saw from a large natural crystal of cassiterite which came from Araca, Bolivia. All samples were found to have the optic axis lying essentially in the plane of their largest face. Polishing was done with several grades of abrasive powders until the best optical finish was obtained.

Measurements were conducted on samples VII, XV, and XVI in their

natural state, i.e. they had received no special treatment which might have changed some of their properties. Also untreated was sample X which received less exhaustive study.

Measurements on samples VI and VIII were conducted before and after oxidation or reduction treatment had been carried out although only room temperature measurements were taken before treatment.

Sample VI was oxidized by heating to between 600° and 700° C in a steady flow of oxygen for fifteen minutes. The entire sample became discolored showing a yellowish tinge. The resistivity of the sample was somewhat higher after treatment which led to the belief that it had actually been reduced rather than oxidized in consideration of the observed resistivity increases which have always followed a known reduction process.

Sample VIII was reduced in a rough vacuum at a temperature of slightly over 600° C for fifteen minutes. This sample also became discolored but had a greenish tinge. The resistivity of the sample was found to have increased considerably after the treatment.

Procedures

In the course of the optical measurements a standard procedure was used on five samples.

For low temperature measurements liquid nitrogen was used as the coolant. In conducting measurements at this temperature the apparatus described above was placed in the sample compartment of the DK-1 Spectrophotometer with the desired sample in the holder. A vacuum of the order of one micron was then obtained by using a mechanical fore pump. Liquid nitrogen was introduced into the coolant chamber while

temperature readings were taken of the sample. A steady state temperature was generally reached after a short period of time, usually from five to ten minutes. However, liquid nitrogen was added during the course of the measurement to ensure that there would be no deviations from the steady state.

In conducting transmission measurements on the spectrophotometer a 100 percent reference line was run prior to running the actual sample curve. This was necessary in case there should be any deviations from the initial setting. In the low temperature work these reference lines were obtained simply by running the instrument through the pertinent range with no sample in the sample holder although the sample holder itself was maintained at liquid nitrogen temperature. The apparatus was then allowed to warm up, the sample was placed in the holder, and the procedure was repeated. These runs were conducted in the region from 0.26 microns to the short wavelength cutoff of the sample.

Low temperature measurements using the Perkin-Elmer Infrared Spectrometer of necessity required a different procedure. The apparatus was held in place by a ring stand and clamp so that the beam originating at the globar would pass through the sample, through the aperture, and finally through the entrance slit of the instrument. A 100 percent reference line is also required with this instrument. However, it differs from that on the spectrophotometer which gives a true 100 percent value with the exception of minor deviations which may be corrected after the measurement is made. The shape of the reference line on the single-beam infrared instrument is a result of the presence of air in the open optical path external to the sample holder and must be precisely known over the entire spectrum to determine the true value of a

sample curve. Values of the percent transmission at a particular wavelength are obtained by taking the ratio of the sample spectrum to that of the reference spectrum and multiplying by 100 percent. To get the reference line the apparatus was cooled as described previously and the instrument was run through the required range. Since a single-beam device was being used, it was possible to mount the sample before determining the reference line which could be run on the blank side of the apparatus leaving the sample side free. After this was completed the entire holder was merely shifted so that the side containing the sample was in the beam. All runs on the infrared spectrometer were made in the region from 2.6 to 4.0 microns.

Room temperature measurements were carried out in the same holder. The procedure described above was followed with the exception that no coolant was used. The vacuum was found to be unnecessary in conducting room temperature measurements. Checks on several samples with both instruments showed that the presence of air in the sample holder had no effect on the spectrum.

High temperature curves were also run using essentially the same procedure as described above with the sample chamber evacuated once again. The high temperature was reached by passing hot nitrogen gas into the inner cylindrical chamber of the apparatus. The nitrogen gas was heated by passing it through a bent vycor tube about five feet long. This tube was wrapped with a heating tape which would reach temperatures in the vicinity of 400° C. The apparatus functioned less efficiently than at low temperatures, since it took from 45 to 60 minutes to reach a stable operating temperature of 140° C. By this time a large portion of the outer jacket of the apparatus had become heated so that the time

allotted to run the spectrum had to be minimized.

Reduction and Representation of Data

As was stated earlier, representation of the data in terms of the optical absorption coefficient involves a thorough knowledge of the index of refraction of the material being investigated. Since experimental data for cassiterite are not available in the region of major interest near the short wavelength cutoff, some assumptions had to be made regarding the dispersion curve in order to calculate an approximate value of the absorption coefficient for these wavelengths.

In Chapter I it was noted that Ecklebe (7) measured the refractive index in the region from 0.444 to 0.715 microns. The results of these measurements are shown in Figure 2. The extension of values for the ordinary ray from 0.444 to 0.240 microns was done with his theoretical relation

$$n^2 = 1.98349 + \frac{1.81642\lambda^2}{\lambda^2 - 3.4633 \times 10^{-2}} \qquad (1)$$

Because the optic axis of the sample was not preferentially oriented with respect to the radiation direction, an average index of refraction of the ordinary and extraordinary rays - their dispersion curves assumed parallel on the basis of results quoted by Cronemeyer (3) for rutile - was used as a reasonable value from which the absorption constants could be calculated for one typical sample. The results of these calculations gave absorption constants of the expected order of magnitude and led to the conclusion that the short wavelength cutoff value could be used as an acceptable criterion for defining the absorption edge. A fuller discussion of this point will be given in the final chapter of the report. The calculated curve for sample VII appears in Figure 3.

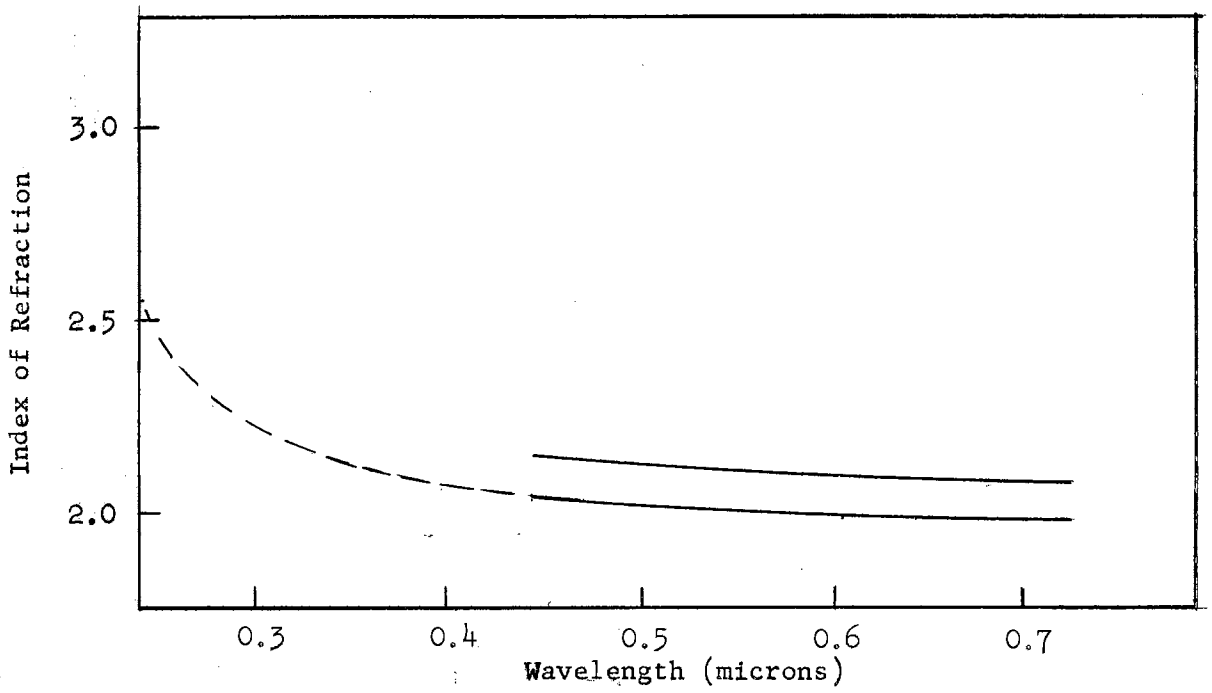

Figure 2. Dispersion Curve (After Ecklebe)

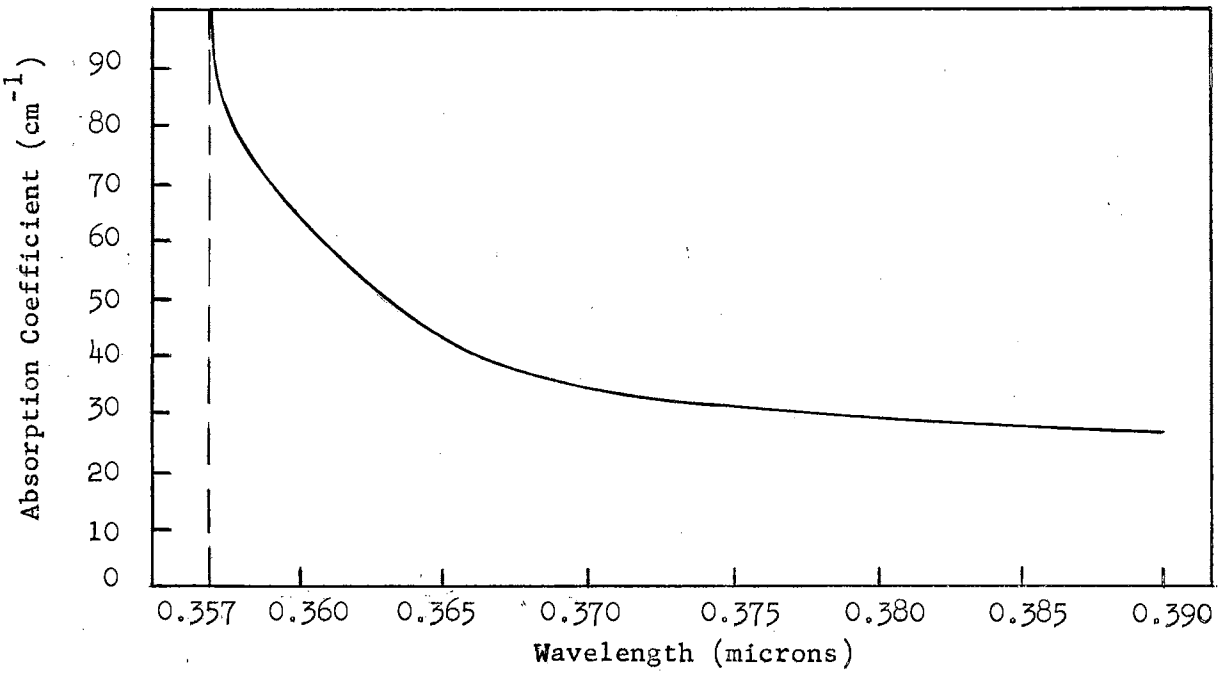

Figure 3. Absorption Spectrum of Sample VII

All of the pertinent data were obtained in terms of percent transmission and are presented graphically in this form.

The data obtained from the Perkin-Elmer Infrared Spectrometer had to be reduced before being transferred to graph paper whereas the Beckman Spectrophotometer gave direct percent transmission values and no reduction was necessary. When these two sets of data were graphed, some instances were observed where the two curves did not match at their junction point. It was found necessary to match these curves in order to have a uniform representation of the results. To do this the curve obtained by using the infrared spectrometer was taken to represent the correct transmission and the one from the spectrophotometer was corrected to match it. The correction was made by first taking the ratio of the value of the transmission from the infrared spectrometer to the value obtained from the spectrophotometer in the region of 2.6 microns and multiplying each value on the rest of the spectrophotometer curve by this ratio. The resultant set of values was used for plotting the graphs.

There is no definite explanation for the mismatch of values but several possibilities can be given. Probably the most significant cause can be attributed to measurements being taken on different areas of an individual sample. When a measurement was taken on a sample it was usually done on one instrument and then the sample was removed from the sample holder, cleaned and remounted for the next measurement. In remounting the sample it would be extremely difficult to place it in exactly the same position as before; and since these samples were not necessarily homogeneous as far as impurities and fractures were concerned it is understandable that there could be a difference in successive measurements.

Another possibility may lie in the different detection methods used on the two instruments. The detector on the infrared instrument consists of a gold leaf blackened target welded to the active elements which make up the thermocouple, while the detector used on the spectrophotometer in the pertinent range is a lead sulfide cell. There is some evidence that the lead sulfide detector is not uniformly sensitive over its entire operating area. If this were the case and if the beam of light passing through the reference channel of the instrument were not being detected on the same area of the lead sulfide cell as the beam passing through the sample channel, a significant difference in transmission values might be observed.

These two reasons individually or together are considered the most probable causes of the differences noted in the results obtained on the two instruments at 2.6 microns.

CHAPTER IV

RESULTS

Variation of the Short Wavelength Cutoff

The short wavelength cutoff was taken to be the wavelength at which the spectrophotometer measured zero transmission through the sample. The cutoff value was found to be temperature dependent for all samples although there were individual differences in the rates of variation. Table I lists the cutoff values at different temperatures for the five samples in which this effect was studied. In Figure 4 these values are plotted in terms of energy versus temperature. An energy shift with temperature of the order of -6×10^{-4} ev/°K is indicated for the untreated specimens. Values at 0° K were determined by extrapolating the curves to the vertical axis. These values are given on the Figure.

TABLE I

VARIATION OF SHORT WAVELENGTH CUTOFF WITH TEMPERATURE

Sample	80°K	300°K	415°K
VI	380 mμ	387 mμ	373 mμ
VII	347 mμ	357 mμ	365 mμ
VIII	390 mμ	380 mμ	382 mμ
XV	344 mμ	356 mμ	362 mμ
XVI	340 mμ	357 mμ	365 mμ

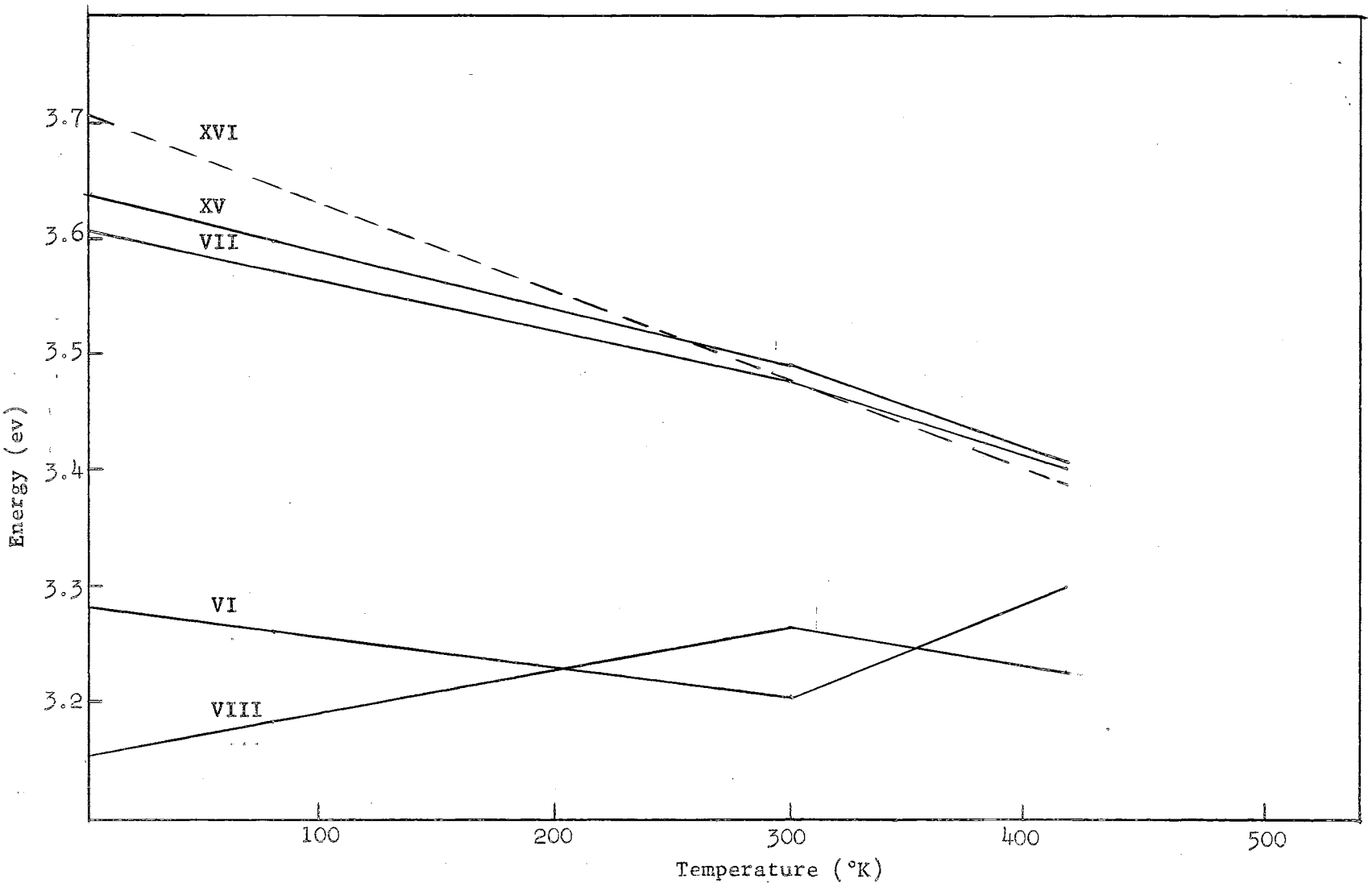

Figure 4. Variation of Short Wavelength Cutoff

Measurements conducted on sample VII at room temperature are represented in terms of the absorption coefficient in Figure 3. The highest value of the absorption coefficient obtained from these measurements is in the vicinity of 90 cm^{-1}. Points for the curve were calculated from transmission data using the assumed index of refraction as previously described. The limiting experimental factor in this case was the inability of the spectrophotometer to detect the very small intensities passing through the 0.9 mm slab at short wavelengths.

Transmission Between Cutoff and 2.6 Microns

Figure 5 shows the three transmission curves of sample VI at 80° K, 300° K, and 415° K. Comparing the curve at 80° K with that at 300° K, it is seen that except for an approximate 10% difference in transmission the shapes of the two curves are essentially the same. A comparison of these two with the curve obtained at 415° K shows that the latter curve has a much steeper slope in the region of the absorption edge.

The results of the measurements on sample VII are given in Figure 6. Except for the approximate 10% difference between the curve at 80° K and the other two, the curves are similar.

The three curves in Figure 7 represent sample VIII at the three temperatures. The outstanding difference between the curve at liquid nitrogen temperature and the one at room temperature is the steepened slope of the room temperature curve near the absorption edge. The room temperature curve and the one at high temperature have essentially the same slope.

The results for sample XV are shown in Figure 8. These curves have

the same character except for slight variations in percent transmission. It should be noted that this sample differs from all the others in the manner in which the absorption edge is approached. In this region the slopes of all three curves are noticeably more gradual than those observed in the other specimens.

The prominent difference in the curves of sample XVI, which are shown in Figure 9, also concerns the manner in which the edge is approached. At liquid nitrogen temperatures the slope of the curve is constant from the cutoff to about 1.7 microns. The other two curves have variable slopes in this region and steepen sharply just before the cutoff.

Absorption at 3.1 Microns

All samples investigated in this study were found to have an intense absorption near 3.1 microns with a weaker satellite absorption at about 3.0 microns. Similar results had been previously obtained on samples cut from other natural crystals which are not included in this report.

The wavelengths at which these absorptions were found varied slightly from curve to curve with the maximum deviation being 0.05 microns. Since these variations were possibly due to limitations experienced in reducing the single-beam transmission data, there is no concrete assurance that they have any other significance. However, in four of the five samples a consistent shift of the peak toward shorter wavelengths occurred as the temperature was reduced. Between 300° K and 80° K the displacement expressed in wavenumbers was of the order of 20 to 40 cm^{-1}. Figures 10 through 14 show the absorption at 3.1

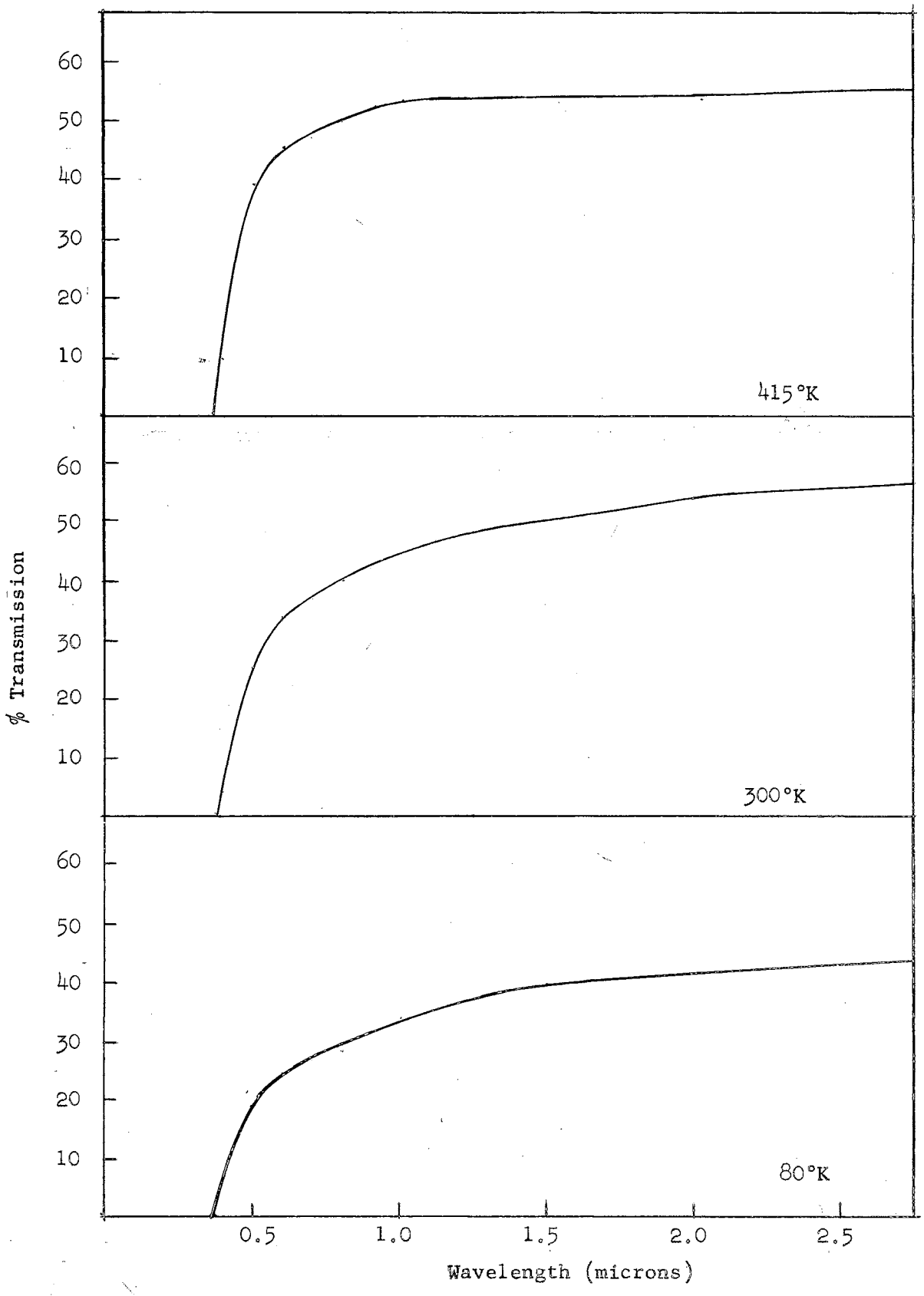

Figure 5. Transmission Spectrum of Sample VI Between Cutoff and 2.6 Microns

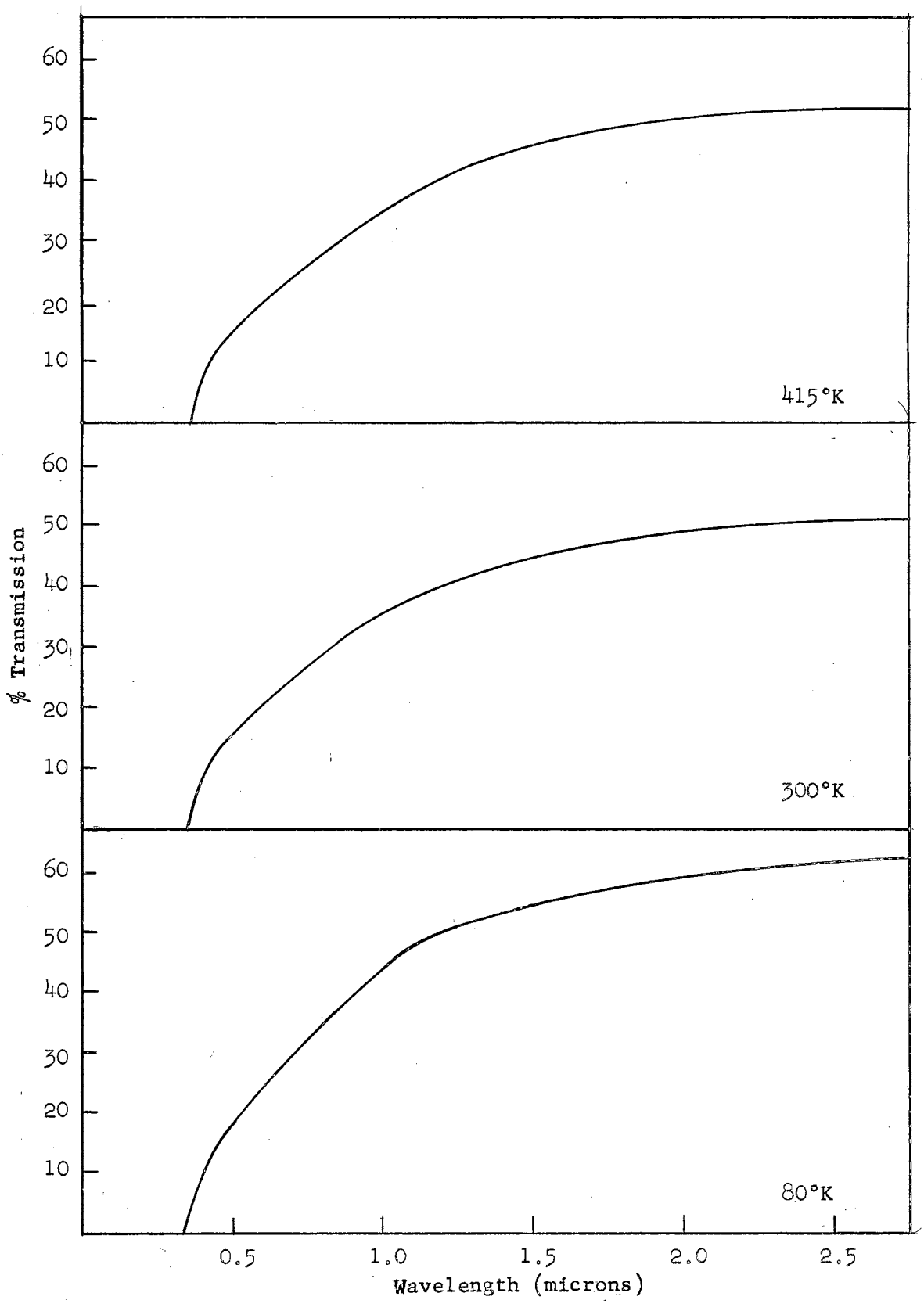

Figure 6. Transmission Spectrum of Sample VII Between Cutoff and 2.6 Microns

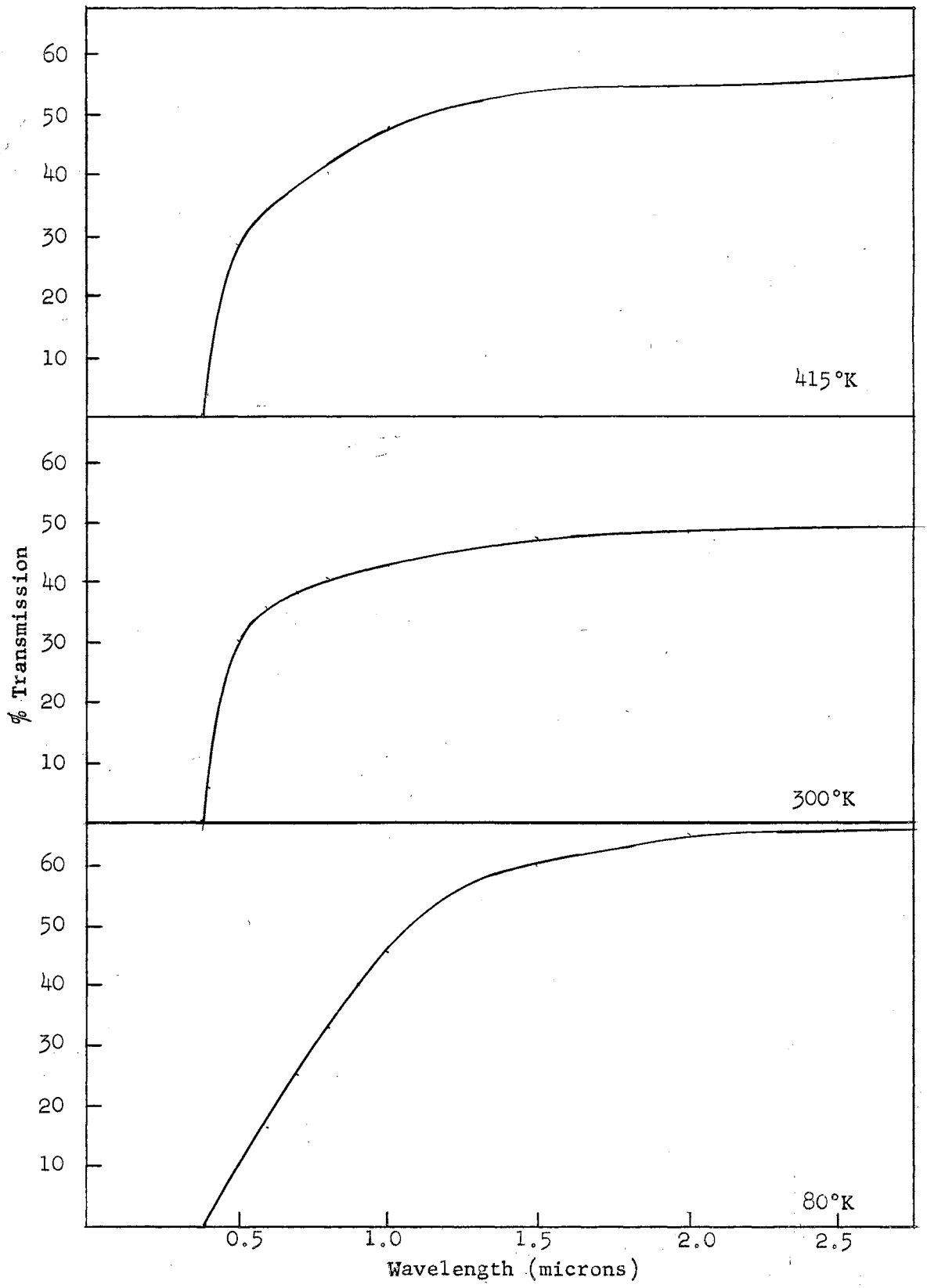

Figure 7. Transmission Spectrum of Sample VIII Between Cutoff and 2.6 Microns

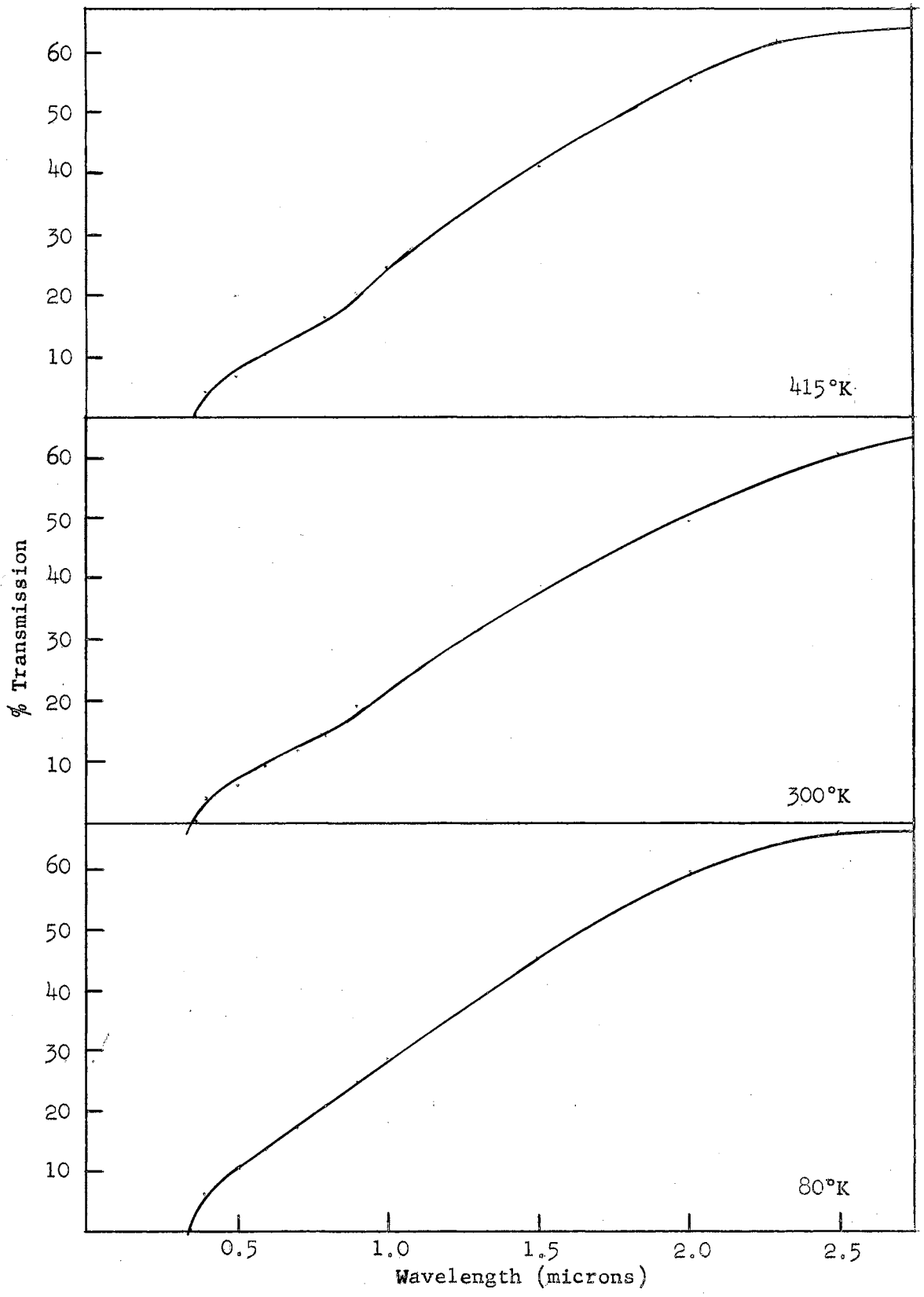

Figure 8. Transmission Spectrum of Sample XV Between Cutoff and 2.6 Microns

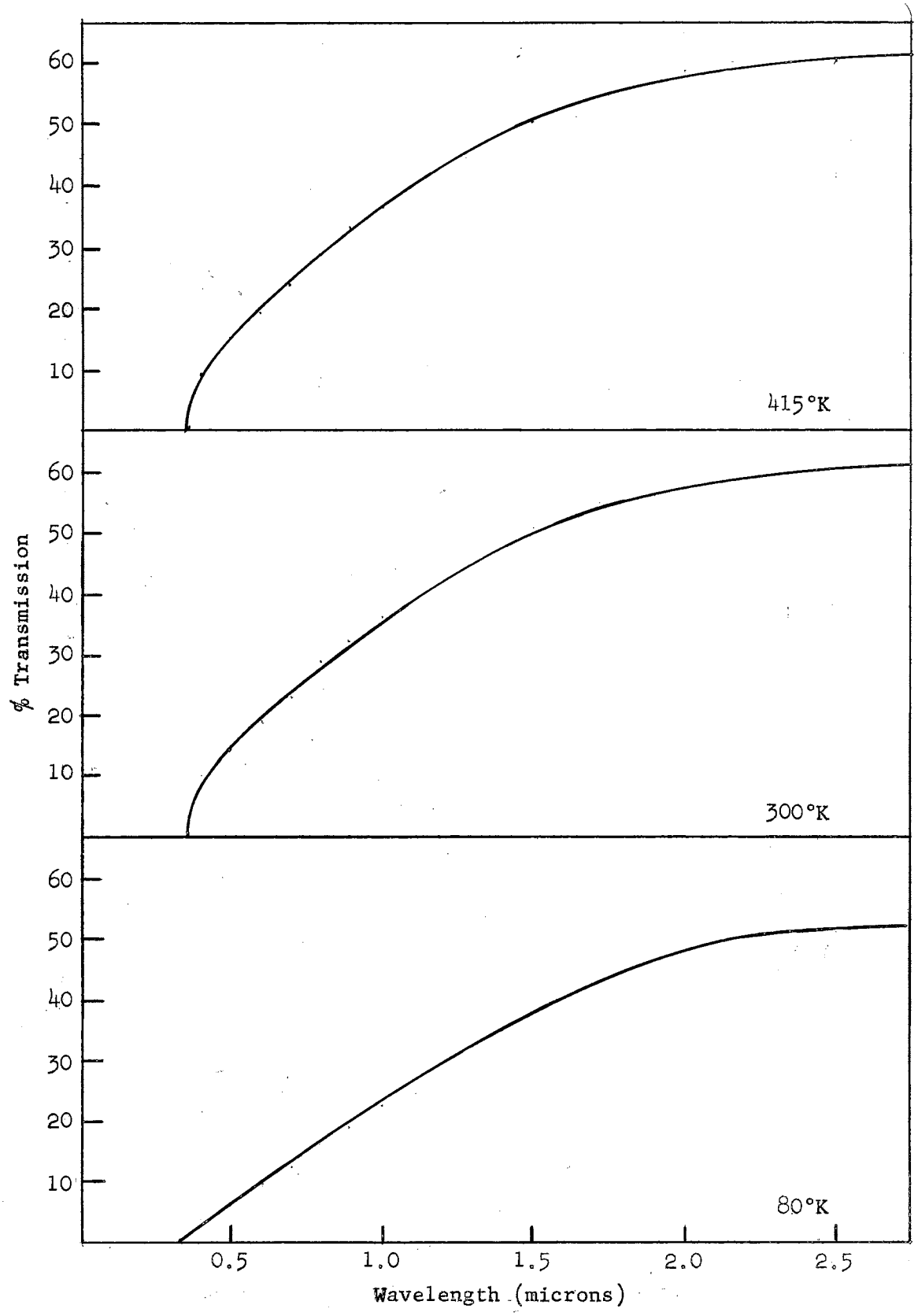

Figure 9. Transmission Spectrum of Sample XVI Between Cutoff and 2.6 Microns

microns for each of the five samples at the three different temperatures. Another obvious feature of the band is the manner in which the satellite absorption becomes intensified at lower temperatures. It is also noticed that the long wavelength shoulder of the main band tends to broaden at low temperatures. In particular, the results on sample VI suggests the emergence of a new satellite absorption which could not be resolved by the instrument.

Figure 15 gives a complete room temperature transmission curve for a representative specimen, sample X, from the short wavelength cutoff or electronic-absorption edge to a long wavelength cutoff beyond 7 microns which is tentatively assumed to be the edge of the highest infrared vibration band. The latter region is presently under additional study and results are not yet available.

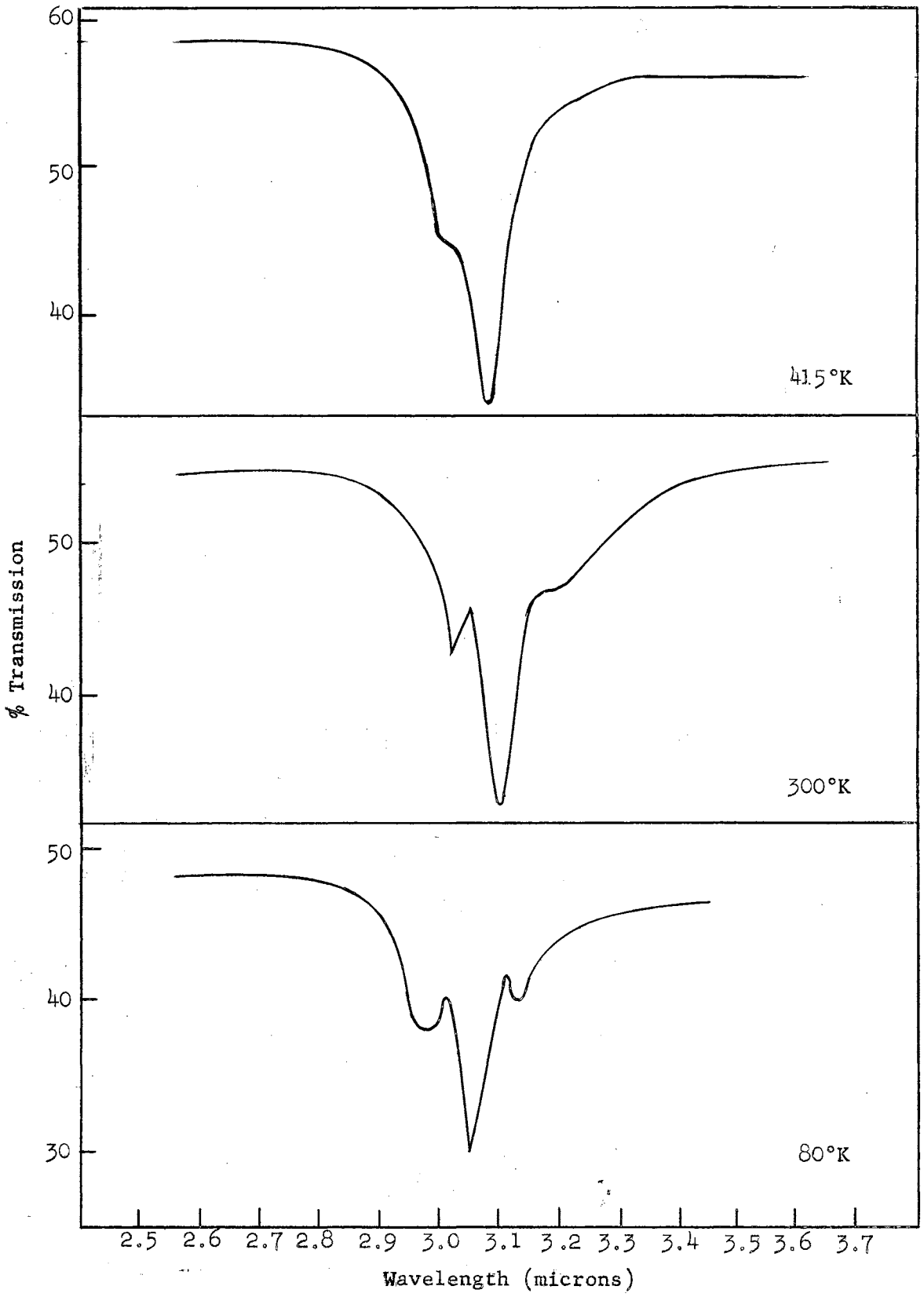

Figure 10. Absorption at 3.1 Microns for Sample VI

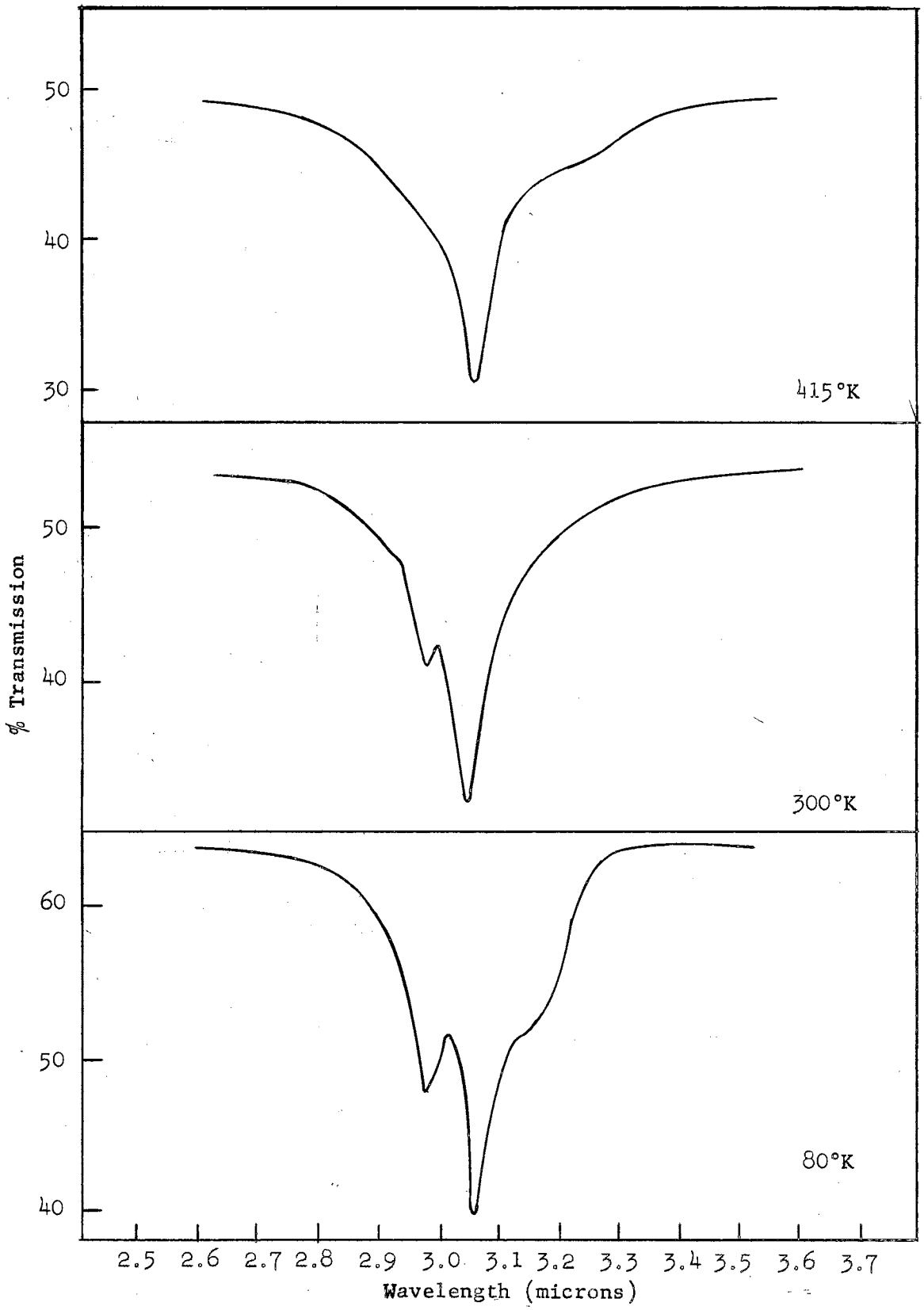

Figure 11. Absorption at 3.1 Microns for Sample VII

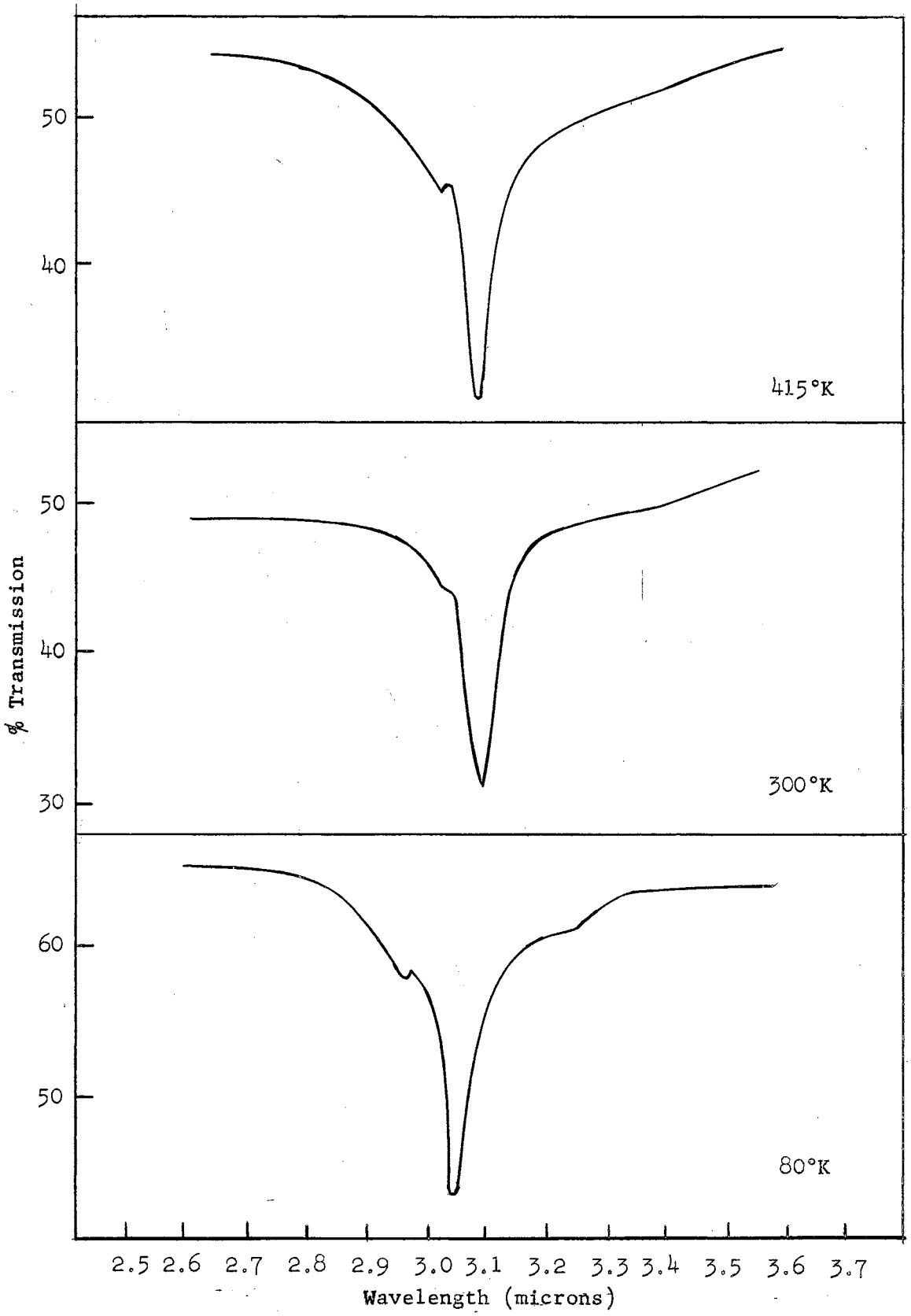

Figure 12. Absorption at 3.1 Microns for Sample VIII

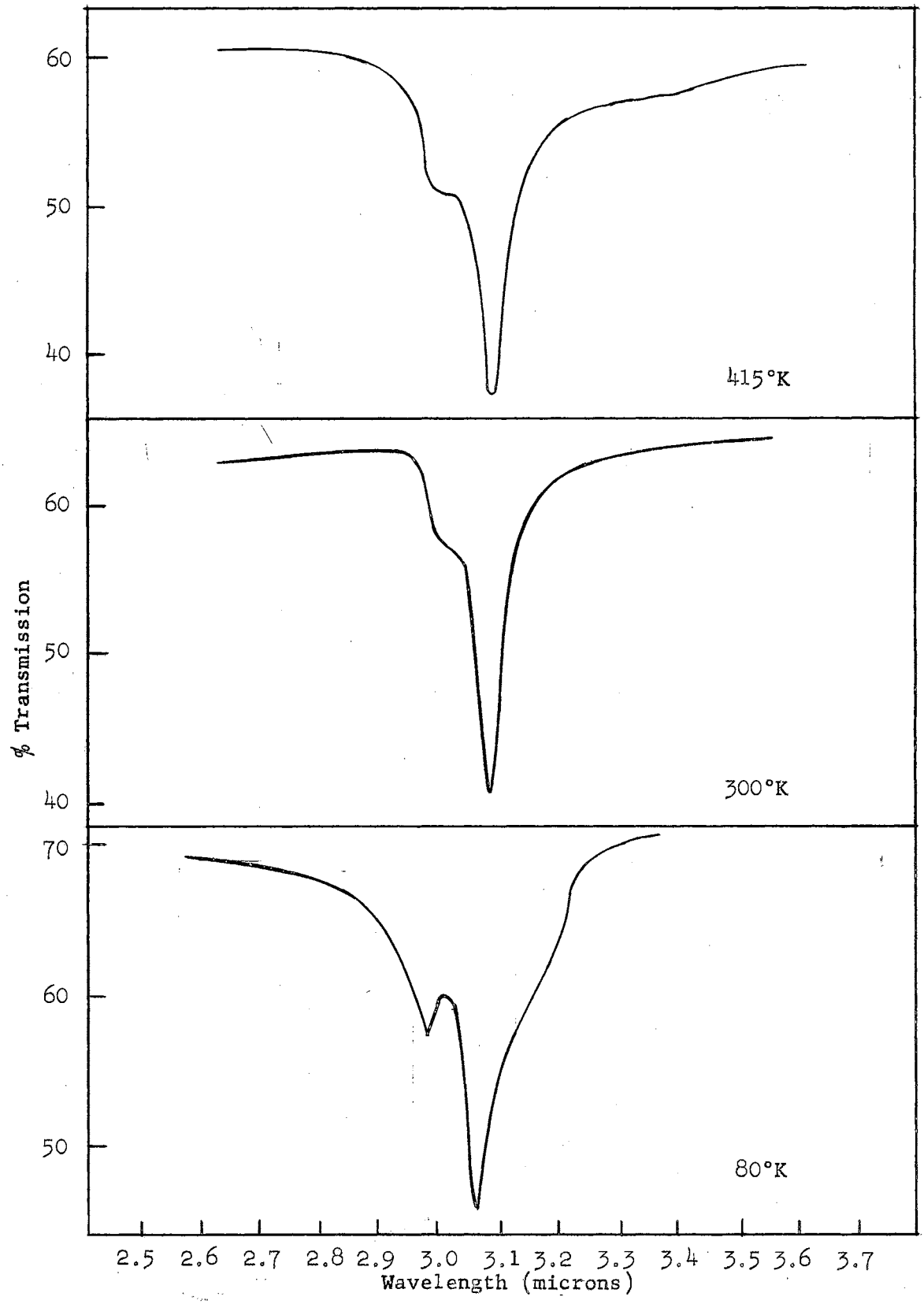

Figure 13. Absorption at 3.1 Microns for Sample XV

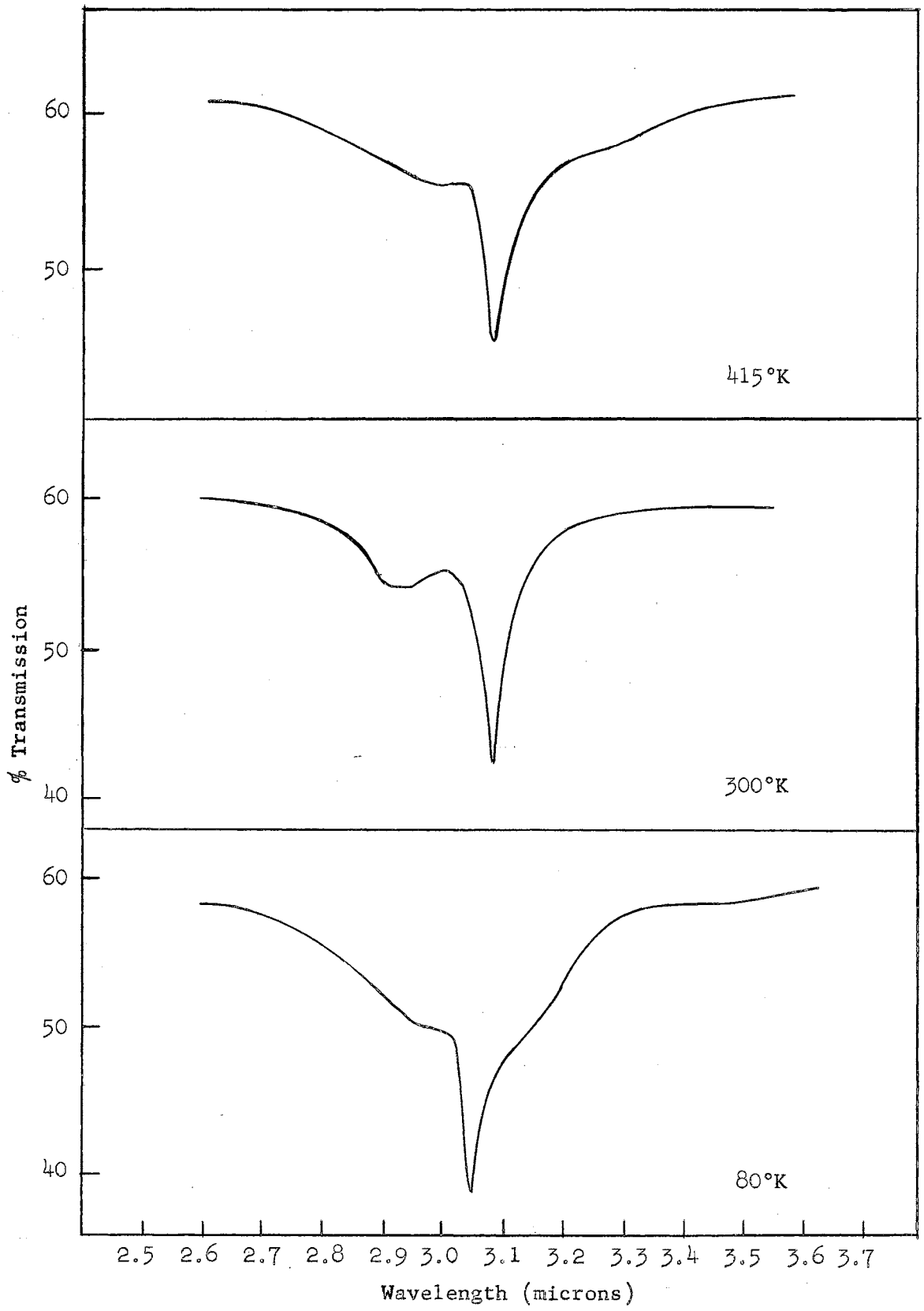

Figure 14. Absorption at 3.1 Microns for Sample XVI

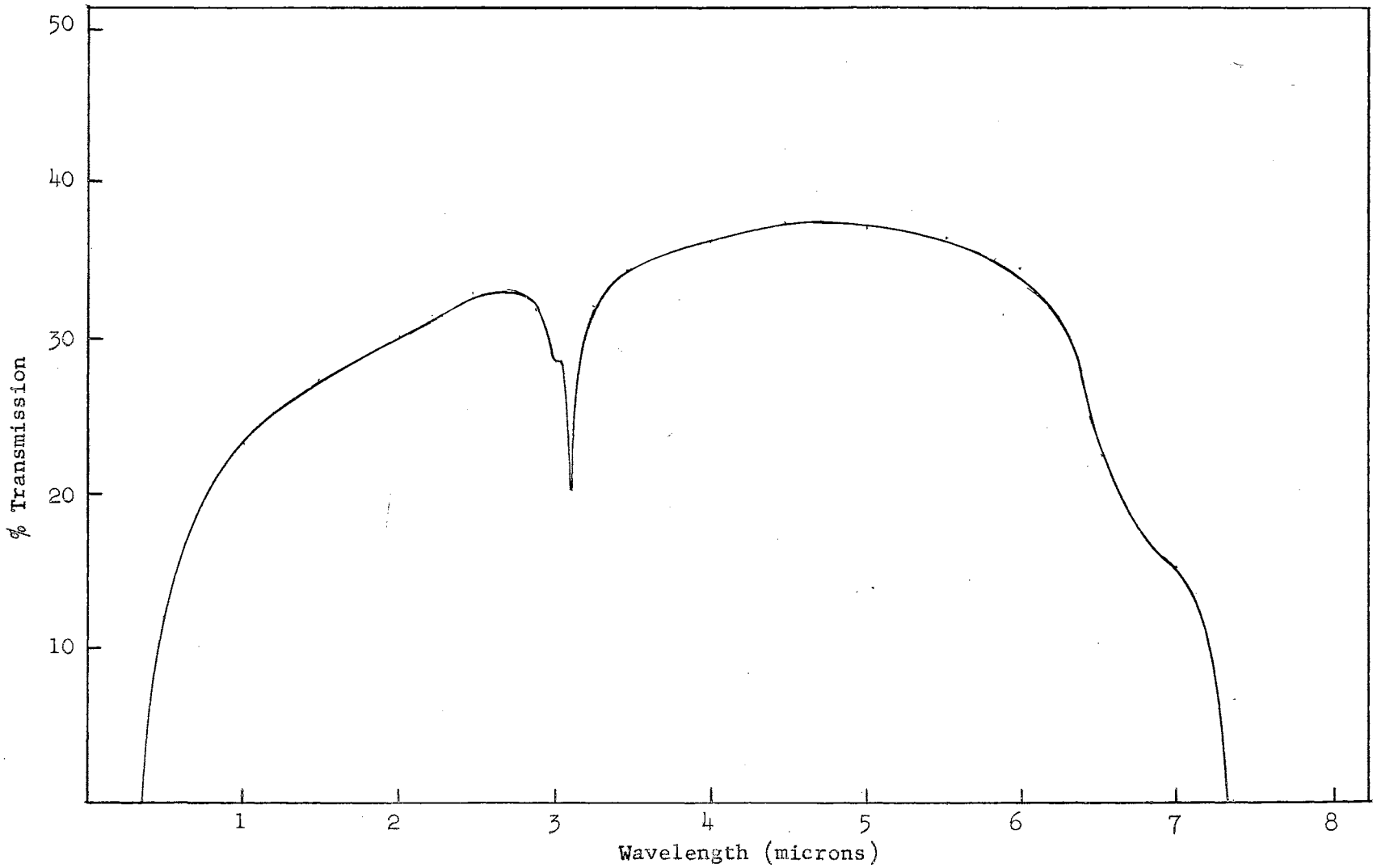

Figure 15. Transmission Spectrum of Sample X

CHAPTER V

SUMMARY AND CONCLUSIONS

Summary

Five samples obtained from a large natural crystal of cassiterite were submitted to optical transmission measurements at three different temperatures in the region from the short wavelength cutoff to 4.0 microns. Observations were made on the value of the cutoff, the variation of the cutoff with temperature, and the nature of the intense absorption found at 3.1 microns. Measurements on a sixth sample have been included to represent a generalization of the transmission spectra from 0.35 to 8.0 microns obtained on a majority of the natural specimens studied since the inception of the project of which this work is a part.

Conclusions

At the beginning of this study it was tacitly assumed that the short wavelength cutoff corresponded to the fundamental absorption edge, the position of which in principle must be determined from the steepness of the slope of the absorption constant with respect to the wavelength. A serious goal of this work has been to test the validity of such an assumption. In Figure 3 the absorption constant for sample VII has been plotted as a function of wavelength. From this curve it is seen that the slope approaches its steepest value near 0.357 microns which is the point observed as the short wavelength cutoff for the sample.

Still it might be thought that this correlation was just a coincidence since there were a number of assumptions made in calculating the absorption coefficient, the most outstanding being the form of the dispersion curve used. Modifications were calculated by using an index of refraction that was either 10% larger or 10% smaller. The new values of the absorption coefficient differed from the old values but it was found that in the region of the absorption edge it would take a much larger change in the absorption coefficient to appreciably affect the slope of the curve. Consequently, it was decided that the short wavelength cutoff defines the absorption edge energy to a satisfactory degree of accuracy.

To reinforce this decision there exists a considerable body of substantiating evidence. Hurt (1) has observed on other cassiterite samples a correlation between peak photoconductivity response and the transmission cutoff. Cronemeyer (3) gives a value of 3.05 ev for the energy gap of rutile, the prototype material of the crystal group which includes cassiterite. Another semiconducting oxide which has been extensively studied, zinc oxide, is reported by Mollwo (11) to have an energy gap of 3.2 ev. A value of 3.47 ev for cassiterite at room temperature may be obtained from Table I using the relation $h\nu = \Delta E$. It is well known that many semiconductors show a variation of energy gap with temperature of the order of a few times 10^{-4} ev/°K. The values of this shift for silicon and germanium have been rather precisely determined. The references quoted above give the shifts for rutile and zinc oxide as -6.3×10^{-4} and -9.5×10^{-4} ev/°K respectively. An inspection of Figure 4 reveals values ranging from -5.3×10^{-4} to -7.1×10^{-4} ev/°K for the energy shift of the short wavelength cutoffs of the untreated

cassiterite samples studied. The implications are clear. The anomalies in the shifts of the treated samples are not understood but may be quite significant and certainly merit further investigation.

The variation of the transmission with temperature between 2.6 microns and the cutoff is difficult to correlate with any absolute parameter of the material. In Chapter IV the shapes of the curves at different temperatures were compared. If any general trend could be distinguished, it was the fact that the steepest slope of a curve approaching the absorption edge occurred at high temperature. This effect was much more noticeable on the samples that had been treated than it was on the untreated ones and thus it is probable that the reduction of the treated samples played a prominent part in its cause. Actually, these two specimens displayed the sharpest approach to the edge observed in the study. Mollwo (11) has reported that the presence of excess zinc in zinc oxide crystals resulted in an additional absorption near the fundamental band edge making it appear strange that reduced crystals of cassiterite which might be expected to contain excess tin behave in a different manner. An explanation of this behavior awaits additional information from combined optical and electrical measurements on the effect of diffused tin in similar samples.

Most natural samples of cassiterite are suspected to contain a high concentration of impurities because of the large range of conductivity values that have been observed (2). Moss has stated (8) that often the impurity absorption in impure semiconductors appears as a wide continuum extending to energies as great as those of the main absorption edge. This might explain the shallow approach to the edge found in most of the samples. However, the complex nature of impurity absorption is beyond the scope of this particular study.

The intense absorption found at 3.1 microns may be caused by hydrogen in the crystal. Soffer (4) in investigating rutile found a similar absorption in this region which he attributed to O-H stretching vibrations. It is difficult to indicate a specific frequency range for the bands produced by O-H absorptions as they are influenced by many things. Frequency dependence is due to the state of the substance in which the bonds exist, the temperature, the nature of the bond, and the numerous other factors (12).

In the present study the absorption was found to occur in the wavenumber region between 3200 and 3300 cm^{-1}. An investigation conducted on crystalline dimethylgloxime by Godychi et al (13) found a strong absorption maximum at about 3.1 microns (3222 cm^{-1}) which was attributed to the O-H fundamental stretching vibration. Subsequently, dimethylgloxime-d_2 was prepared by recrystalizing the parent compound from heavy water and a strong O-D absorption was then found at about 4.2 microns substantiating the hypothesis. Similar substitution experiments have also been conducted on rutile with positive results. It was unfortunate that there were no means available during the existing study for deuterium substitution since it could have produced experimental evidence to strengthen the supposition of hydrogen in cassiterite crystals. The apparent shift of the absorption toward shorter wavelengths with decreasing temperature agreed in direction and order of magnitude with Soffer's results on rutile to lend additional support, however.

It was mentioned earlier that the long wavelength shoulder of the main band broadened at low temperatures but that this broadening might be due to a new band which was not resolved by the instrument. There is evidence to indicate that such an unresolved band may be caused by

the presence of condensed water vapor on the surface of the crystal. Some difficulty was experienced in conducting the low temperature measurements because of condensation. Instances occurred when the entire 3.1 micron band broadened to at least six times the normal width and the absorption peak was greatly intensified. After careful efforts to reduce all possible water contamination these curves were run again. The results proved that water had caused the broadening and it is quite possible that its effects were never entirely eliminated.

Suggestions for Further Study

Throughout the report several areas which warrant further investigation have been mentioned. Measurements of the ultraviolet index of refraction, the Hall constant, the electrical and optical changes caused by the presence of diffused tin in natural samples, and the variation of the long wavelength cutoff with temperature are either under way or in the planning stage.

Many problems which have arisen would be solved by the availability of large synthetic single crystals of stannic oxide. Specimens could be cut to any desired orientation and their impurity concentrations more closely controlled. A specific program is in progress to attain such crystals by a hydrothermal growth method.

Transmission measurements using polarized light would be particularly useful in the long wavelength region of the sample spectra. However, any concentrated work awaits the time when oriented crystals can be used.

The long-range project of which this study is a part will soon have at its disposal a double-beam Beckman IR-7 Infrared Spectrophotometer.

The increased resolution and extended wavelength range of this instrument will be used to more precisely define the reported absorptions and to inspect the transmission spectrum beyond 14 microns.

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